2 Analysis of Variations in Ozone & Ozone Precursors

2.1 Diurnal Patterns of Ozone and Precursors in the South Coast Air Basin

2.1.1 Abstract

This chapter is a summary of the diurnal (hour-by-hour) variations observed in concentrations of ozone, carbon monoxide, and oxides of nitrogen, as well as in NO_2/NO ratios, in the South Coast Air Basin by day of the week during the summers of 1994 and 1998. The diurnal variations are examined for consistency with each Weekend Effect Hypothesis. The plausibility of a Weekend Effect Hypothesis is improved if it explains (or is consistent with) the observed temporal and spatial variations in the parameters. The diurnal variations of secondary pollutants appear to have changed with the introduction of cleaner burning fuels in 1995.

The diurnal patterns observed, within spatial groupings, are consistent with the NO_X-Reduction Hypothesis and the NO_X-Timing Hypothesis. The diurnal profiles observed tend to oppose the Carryover at Ground Level Hypothesis and the Increased Emissions Hypothesis. The evidence is largely moot concerning the other hypotheses.

2.1.2 Background

We examined diurnal patterns of ozone and other pollutants in the South Coast Air Basin (SoCAB) during 1994 and 1998 for weekday-weekend differences. We generated average diurnal profiles of pollutant concentrations by day-of-week groups for each site in the South Coast Air Basin reporting data for the May-October periods in 1994 and 1998. We examined pollutant concentration data for ozone, oxides of nitrogen (NO_X), non-methane hydrocarbons (NMHC), and carbon monoxide (CO). Data from 29 ozone monitors, 22 NO_X monitors, and 20 CO monitors in the South Coast Air Basin (SoCAB) were available for analysis and the diurnal variations are described below. However, NMHC data were only available from a few sites and for 1994 only. Because the coarse resolution of the NMHC data tended to obscure day-of-week differences, the NMHC results are not presented. However, a diurnal profile of the total hydrocarbon concentrations at Los Angeles-N. Main in 1994 will be presented to provide a general characterization of this ozone precursor.

This chapter is a summary of the analytical results for the summers of 1994 and 1998. We selected these years for analysis based on a recent analysis (Austin and Tran, 1999) by staff of the Air Resources Board (ARB). That analysis found an ozone weekend effect at many sites throughout California, with Saturday typically having the highest concentrations in 1992-1994, and Sunday typically having the highest concentrations in 1996-98. We selected the South Coast Air Basin for more

detailed analysis because that air basin has high ozone concentrations and a large number of monitoring sites in a variety of settings. This chapter also presents the average diurnal profiles of nitrogen dioxide (NO_2) to nitric oxide (NO) ratios (i.e., NO_2/NO ratios) in the SoCAB. NO_2/NO ratios provide an indication of the relative balance in NO_X species directly pertinent to the photochemistry of ozone formation. When the ratio is low, fresh NO_X emissions (predominately NO) dominate the atmospheric mix and ozone destruction by NO is likely to exceed ozone formation by NO_2. The NO_2/NO ratio is an important factor in the photostationary equilibrium state for ozone but other factors such as solar actinic flux and temperature are important factors in determining ambient ozone concentrations. It should also be reiterated that the NO_2 data presented here are not truly nitrogen dioxide measurements but the difference between NO_X (NO_Y) and NO and therefore includes additional oxidized nitrogen species such as PAN.

2.1.3 Methodology

To construct the diurnal profiles, we grouped the concentration data by day of week and averaged over each hour of the day. Therefore, the value of a diurnal profile for Saturday, at 5 a.m., is the mean of all 5 a.m. PST concentrations over all Saturdays for a given site and year, from May through October. We also plotted and examined individual daily profiles for data outliers, to ensure that the average diurnal profiles were not unduly influenced by anomalous observations. We constructed separate diurnal profiles for each site and each of the two years studied. We plotted the site-specific diurnal profiles (mean hourly concentration plotted against time of day) with all seven days of the week superimposed on one figure. Weekdays, Monday-Friday, generally behaved similarly, with some exceptions noted below. The individual weekdays, particularly Tuesday-Thursday, could be averaged together to obtain a “typical weekday” profile in future analyses. Each daily profile typically represents 26 days of data.

An analogous procedure was followed to generate the NO_2/NO ratio data. However, prior to taking averages for the NO_2/NO ratios, we transformed the data according to the relationship $y = \log(x + 0.5 \text{ ppb})$ to guard against zeroes and small values in the denominator of the ratio. The offset of 0.5 ppb represents ½ the lower limit of detection (LOD) of the analytical method for NO and NO_2 . By adding this offset, the variability of the ratios is reduced considerably at the cost of a slight bias towards lower ratios. We computed mean ratios of the transformed concentrations by site, year, day-of-week and hour-of-day, and then back-transformed by exponentiating. The resulting means are therefore approximately the geometric means.

We examined the diurnal profiles for spatial consistency among the sites and differences between the two years. The years contrasted (i.e., 1994 and 1998) were chosen to represent conditions before and after the introduction of cleaner burning motor vehicle fuels in 1995. We obtained our data from the ADAM database, the ARB's repository for criteria air pollution data.

2.1.4 Results

Brief descriptions are presented below to characterize overall air quality patterns in the South Coast Air Basin. To be included in the description, a pattern had to be present at several sites. A given site, in a given year, may lack some of the characteristics described.

2.1.4.1 Ozone (O_3)

Ozone is not a directly emitted pollutant but forms after photochemical reactions involving volatile organic compounds and oxides of nitrogen. Ozone is rapidly destroyed upon contact with nitric oxide (NO), a major pollutant from fuel combustion sources. Thus, the ozone concentrations in urban areas tend to be low during the night (no production, only destruction) and highest during the early afternoon (rapid production). In rural/remote areas (e.g., mountains, desert) with small NO sources, ozone concentrations can remain high throughout the night. Peak ozone concentrations were almost uniformly lower in 1998 than in 1994 for all days of the week. This reduction in ozone concentrations includes not only the response to emission controls but also includes the effect of meteorological differences between the two years. Ozone diurnal profiles are presented in Figures 2.1-1 through 2.1-20 by monitoring site and year.

2.1.4.1.1 Day-of-Week Characteristics

At the vast majority of sites, the peak ozone concentrations tended to occur on Saturdays in 1994 but on Sundays in 1998. The average peak ozone concentrations on weekdays were generally similar to each other and distinctly lower than on weekends. The weekday-weekend difference in peak ozone concentrations is less pronounced at Banning (Figure 2.1-6), a far downwind site, and Hawthorne (Figure 2.1-10), a near coast site.

2.1.4.1.2 Diurnal Characteristics

Except at the far downwind sites (e.g., Lake Gregory (Figure 2.1-12), Banning (Figure 2.1-6), Lake Elsinore, Santa Clarita), morning ozone concentrations increase earlier on Sunday, and on Saturday to a lesser extent (more so in 1998 than 1994), than on the weekdays. Non-urban sites (e.g., Lake Gregory (Figure 2.1-12)) tend to exhibit ozone carryover at ground level throughout the night (i.e., ozone is not completely scavenged by NO emissions during the night). Reduced titration of ozone may be a factor in the more rapid build-up of ozone concentrations around 6 a.m. on weekends than weekdays at some sites (e.g., Banning, Figure 2.1-6). However, at most sites on all days of the week, the early morning ozone concentrations are similar. Thus, the more rapid and general build-up of ozone concentrations after sunrise on weekends appears to be more related to chemistry (e.g., fewer radicals are terminated by reaction with NO_X products on Sundays than on Saturdays than on weekdays).

Another interesting feature we observed frequently in 1994 but not in 1998 was a morning "crossover" in the diurnal profiles of ozone concentrations on Saturday and Sunday (e.g., Azusa, Figure 2.1-3). Although ozone concentrations at sunrise are generally similar by day of week at many urban sites in the SoCAB, ozone concentrations tend to increase faster on Sundays compared to Saturdays compared to weekdays. However, during 1994 the ozone concentrations on Saturday often "overtook" the concentrations on Sunday by 11 a.m. or noon. In 1998, this "crossover" of ozone concentrations on Saturday and Sunday did not occur or occurred mid-afternoon or later. In fact, the mid- to late-afternoon ozone concentrations on Saturdays and Sundays were often identical, whether in 1994 or 1998. The difference between the 1994 and 1998 ozone patterns on Saturday and Sunday appears primarily due to a faster decrease in mid-day concentrations on weekdays and Saturdays than on Sundays. It is unlikely that activity patterns changed from 1994 to 1998 so the shift likely is in response to changing chemistry. Based on mid-day NO_X concentrations being greater on Saturday than on Sunday, perhaps the mid-day NMHC/NO_X ratio shifted from a NO_X-limited regime in 1994 to a VOC-limited regime in 1998. Although Sunday is the peak ozone day in 1998, Sunday is also the lowest NO_X day. In the absence of transport, this pattern indicates that ozone formation on Sundays has a faster start with the smaller amount of fresh NO (e.g., Los Angeles NO_X, Figure 2.1-47). This pattern is consistent with the NO_X-Reduction hypothesis.

In most of the air basin, the ozone peaks on Saturday and Sunday occur about the same time of day as the mean weekday peak, or perhaps slightly earlier in some cases in 1998. In the eastern part of the basin, in the San Bernardino and Riverside areas, ozone concentrations on Saturday and Sunday tend to peak 0-1 hour later in 1994 and 1-2 hours later in 1998 than the corresponding weekday peaks. At most sites, the ozone peak (whether weekend or weekday) occurs 1-2 hours later in the day in 1998 than the same day of the week in 1994. This slower peaking of ozone concentrations in 1998 than in 1994 could be explained by fewer, or less reactive, hydrocarbon emissions in 1998 compared to 1994. One exception to this pattern was Anaheim (Figures 2.1-1 and 2.1-2) where concentrations peaked earlier on Sunday in 1998 than they did in 1994. However, the time of the Saturday ozone peak shifted later from 1994 to 1998. The time of the ozone peak also remained the same from 1994 to 1998 at several sites near the San Gabriel and San Bernardino Mountains (e.g., Pasadena, Glendora, Lake Gregory).

2.1.4.2 Carbon Monoxide (CO)

Carbon monoxide is a directly emitted (primary) pollutant from fuel combustion sources. CO is much less reactive than ozone and its concentrations are strongly influenced by atmospheric stability. Motor vehicles are the dominant source of CO emissions. CO concentrations are greatest when the air is cool and stable (e.g., winter, surface inversion, light winds) and traffic is congested (e.g., commute periods). As was observed with the ozone concentrations, the CO concentrations in 1998 were lower than in 1994 for every day of the week. Once again, this difference is a combination of emission controls and different meteorology. Carbon monoxide

diurnal profiles are presented in Figures 2.1-21 through 2.1-36 by monitoring site and year.

2.1.4.2.1 Day-of-Week Characteristics

Although CO concentrations are low during the summer, day-of-week patterns are still apparent in the diurnal profiles. Almost all sites exhibit significantly lower CO concentrations during the morning commute period on Sundays. The morning CO peak also tends to be lower on Saturday than on weekdays although not substantially lower at many sites, particularly in 1998. By mid-day, the weekend concentrations are not very different from the weekday concentrations at most sites (N. Long Beach is the most notable exception). Interestingly, at Lynwood, the site with the highest CO concentrations in the SoCAB, mid-day CO concentrations in 1998 were higher on Saturday than any other day of the week (Figure 2.1-32). Several sites also exhibited a tendency for higher CO concentrations on Friday and Saturday evenings (e.g., Lynwood, Figure 2.1-32). In many locations, these slightly higher concentrations carry over into the early morning hours of the following day. However, the day-of-week differences are generally negligible by 4 a.m. PST. Thus, the less reactive CO pollution (compared to the ozone pollution) also does not support the boundary layer component of the Carryover Hypothesis.

2.1.4.2.2 Diurnal Characteristics

The ubiquitous automobile and the predominance of ambient monitoring in urban areas causes the diurnal profiles of CO concentrations to be very similar in shape from site to site and year to year. Concentrations exhibit a morning peak, an afternoon minimum, and a build-up in the evening. During the summer, diurnal CO concentrations tend to increase rapidly during the morning commute period but also dissipate rapidly as sunshine brings greater dispersion after 7 a.m. PST. CO concentrations are lowest in the early afternoon when atmospheric dispersion is greatest and CO emissions smaller. CO concentrations begin to increase with the evening commute period and into the late evening as the atmosphere becomes more stable. During the winter, this evening peak is comparable in magnitude to the morning peak and has longer duration. However, the longer days of summer (more dispersion later into the evening) allows the traffic volumes to decrease before the surface inversions begin forming. Thus, the evening CO peak is universally smaller than the morning CO peak during the summer.

2.1.4.3 Oxides of Nitrogen (NO_X)

NO_X emissions result from high-temperature combustion. Most is initially emitted as nitric oxide (NO) with some nitrogen dioxide (NO_2). Through reaction with O_3 or photochemical reactions involving volatile organic compounds and free radicals, the NO is oxidized to NO_2, which upon photolysis, is the only known source of free oxygen available for the formation of ozone. Thus, NO_X is an important precursor in the formation of ozone. The sum of the NO and NO_2 concentrations is called oxides of nitrogen (NO_X). In reality, most NO_X monitors also measure some additional

nitrogenous oxidation products although not all of them because many are very reactive and others tend to stick to the sampling lines. To reduce the uncertainty regarding what the NO_X (and NO_2) measurements really represent, newer instruments, with catalytic converters positioned immediately after the monitoring line inlet, record total reactive oxides of nitrogen (NO_Y). NO_X and NO_Y measurements tend to be similar during nighttime and to diverge (i.e., $NO_Y > NO_X$) during the photochemically active period of the day.

The magnitude of the NO_X concentrations varies from site to site but the diurnal patterns are usually similar. Concentrations in 1998 were almost uniformly lower than in 1994. Once again this decrease is a combination of emission controls and meteorological factors. Oxides of nitrogen diurnal profiles are presented in Figures 2.1-37 through 2.1-53 by monitoring site and year.

2.1.4.3.1 Day-of-Week Characteristics

Although NO_X concentrations are lower during the summer than during winter, day-of-week patterns are still apparent in the diurnal profiles. Almost all sites exhibit the lowest NO_X concentrations on Sunday with the difference being most obvious during the morning commute period. Saturdays tend to have lower concentrations than the weekdays but not as low as Sundays (particularly during the morning commute period). Saturday afternoon concentrations are comparable to or slightly lower than weekday concentrations. There is some evidence of variability among weekdays with Mondays and/or Fridays exhibiting the peak concentrations during the morning commute and Fridays tending to exhibit the highest concentrations during the evening (e.g., Los Angeles, Figure 2.1-47, and Lynwood, Figure 2.1-49). This is consistent with the common perception that driving activity is higher on Friday evenings.

For the most part, NO_X concentrations tend to peak at the same time in the morning, irrespective of the day of the week. However, the time of the nitrogen dioxide (NO_2) concentration peak (Figures 2.1-71 through 2.1-87) tends to occur an hour earlier on weekends than on weekdays at several sites (e.g.; Azusa, Figure 2.1-74; Burbank, Figure 2.1-77; Riverside, Figure 2.1-85). At some sites (i.e., Hawthorne, Figure 2.1-79; LaHabra), this earlier peaking of the NO_2 concentrations compared to weekdays only occurs on Sunday.

2.1.4.3.2 Diurnal Characteristics

NO_X concentrations peak during the morning commute period. With improving atmospheric dispersion, the morning NO_X concentrations begin to decline mid-morning and reach a minimum in the early afternoon.

At mid-day and through the afternoon, the weekend NO_X concentrations remain slightly lower than the weekday NO_X concentrations. At Lynwood, the mid-day NO_X concentrations on Saturday in 1998 were indistinguishable from any other day of the week. In general, the Sunday concentrations were uniformly lower than other days

except during the midnight to 4 a.m. period (when they are comparable with weekday concentrations). Since there is generally more atmospheric dispersion in the afternoon, the same rate of emission tends to result in lower concentrations in the afternoon than in the morning. Therefore, as an indicator of differences in emission levels on different days, a small difference between profiles in the afternoon may be as significant as a large difference in the morning.

With the evening commute and more stable atmospheric conditions, NO_X concentrations tend to increase in the evening. Several sites also exhibited a tendency for higher NO_X concentrations on Friday evenings and a weak tendency for higher concentrations on Saturday evenings (roughly equal to or higher than the mean weekday evening concentrations). In many locations, these slightly higher concentrations on Friday evening carried over into the early morning hours of Saturday. However, any day-of-week differences were negligible by 4 a.m. PST. This pattern does not indicate that carryover in the night-time boundary layer is a viable hypothesis for explaining the Weekend Effect.

2.1.4.4 NO_2/NO Ratio

In theory, the NO_2/NO ratio provides a crude indication of the chemical state of the atmosphere and its ability to generate significant ozone concentrations. Low ratios indicate that NO emissions are accumulating faster than the NO is being oxidized to NO_2. Thus, ozone concentrations will be suppressed because the ozone will be scavenged by reaction with the NO. High ratios indicate that the air mass is aged (i.e., NO has been converted to NO_2) or that the rate of NO oxidation is exceeding the injection of fresh emissions. In this regime, photolysis of the NO_2 yields an oxygen atom, which can form ozone, and a NO molecule, which can be oxidized to NO_2 by the VOCs present.

However, a word of caution is appropriate for interpreting NO_2/NO ratios. While the NO_2/NO ratio reflects the conversion rate of NO to NO_2, it is also affected by losses of both species due to deposition, reaction, etc. NO_2/NO ratios, by themselves, are generally not considered a reliable indicator of radical formation or ozone formation rate. Moreover, because NO_2 is computed by subtracting a directly measured NO concentration from a directly measured NO_X concentration, and NO_X measurements are affected by the presence of nitric acid and other species, there is considerable measurement uncertainty. This is particularly true of afternoon NO concentrations, which approach the lower sensitivity limit of the measuring instrument. While due care was taken in the statistical analysis to minimize the impact of low NO concentrations, more investigation into the effect of measurement interference on NO_2/NO ratios is needed.

Most sites showed an increase of 50-100% in peak ratios from 1994 to 1998, although a few sites decrease by as much as 20%. This is mainly due to a drop in afternoon and evening NO concentrations in 1998. Afternoon NO concentrations tend to be close to the instrument's level of detection (LOD). Diurnal profiles of

NO_2/NO ratios are presented in Figures 2.1-54 through 2.1-70 by monitoring site and year.

2.1.4.4.1 Day-of-Week Characteristics

At almost every site, Sunday NO_2/NO ratios are markedly higher than other days around 6-9 a.m. Saturday 6-9 a.m. ratios are generally higher than the corresponding weekday ratios but lower than the Sunday ratios. Morning NO and NO_2 concentrations are generally lowest, by a considerable margin, on Sunday, with Saturday concentrations intermediate between Sunday and weekdays. The high NO_2/NO ratios on weekends are due mainly to the sharp drop in morning NO concentrations.

Several interesting differences were noted betweenNO_2/NO ratios in 1994 and those in 1998. In 1994, about one-fourth of the sites show a "Sunday afternoon trough", with Sunday NO_2/NO ratios lower than other days of the week from around 12-6 p.m. However, this was less evident in 1998. Similarly, early morning (12-5 a.m.) NO_2/NO ratios were highest on Monday at most sites in 1994 but the Monday peak was not evident in 1998. Lastly, Friday has the lowest NO_2/NO ratio from 6-9 a.m. at most sites; while the difference between Friday and other weekdays is small, the pattern is consistent among almost all sites) in 1994 but not in 1998. However, in 1998, evening (5-11 p.m.) NO_2/NO ratios were the lowest on Friday at about half the sites.

2.1.4.4.2 Diurnal Characteristics

Similar to diurnal profiles of ozone, the diurnal profiles of the NO_2/NO ratio exhibit a sharp increase starting around 7-8 a.m. PST and a peak around noon. NO_2/NO profiles at most sites exhibit a second cusp (frequently slightly higher than the midday peak) around 6 p.m. This pattern is consistent with a more oxidized atmosphere but it is not known whether the increase is actually in NO_2. It is likely that the “NO_2“ measurement also includes other oxidized NO_Y species. Ratios generally decrease during the night until reaching a minimum at 6 a.m. the next morning. Site by site, peak NO_2/NO ratios range from around 2 to 30, with 10-15 being typical. Ratios at sites on the western side of the SoCAB tend to have broad late-morning into mid-day peaks that are dominant (e.g., Burbank, Figures 2.1-59 and 2.1-60) while ratios at sites in the eastern part of the basin tend to have late-afternoon into evening peaks that are dominant. Atypical profiles are observed at Burbank (Figure 2.1-59) and Lynwood (Figure 2.1-65), which exhibit primarily a late morning peak, and N. Long Beach, which exhibits primarily an evening peak. The peak ratio at Lynwood in 1998, in particular, is extremely low relative to other sites (Figure 2.1-66).

A transition from similar late-morning and early-evening peaks in 1994 to larger early evening peaks in 1998 is evident. At some sites (Azusa, Figure 2.1-57; Hawthorne, Figure 2.1-62; Pico Rivera, Los Angeles, Figure 2.1-64; Riverside, Figure 2.1-68; San Bernardino, Figure 2.1-70), the evening NO_2/NO ratio peak is markedly higher than the morning peak in 1998. This may be an artifact of our methodology for

handling ratios with low concentrations as the early-evening NO and NO_2 concentrations are low (at the LOD) and were generally the same or slightly lower in 1998 compared to 1994. Another potential factor is increased oxidation species in the NO_2 measurement.

The difference between the ratio profiles on weekends (particularly Sundays) and weekdays was enhanced from 1994 to 1998 at most sites, primarily in the central basin. NO_2/NO ratios were typically higher on the weekend than on the weekday; the most notable exception is at Riverside where the NO_2/NO ratios are lower on weekends than on weekdays (Figure 2.1-68).

2.1.4.5 Total Hydrocarbon (THC)

Hydrocarbon emissions result from evaporation and incomplete combustion. Methane is by far the most abundant hydrocarbon with background concentrations on the order of 1.7 ppmC. Fortunately, methane reacts very slowly to form ozone and realistically only affects global background concentrations of ozone.

Continuous measurements of THC are only available for a handful of sites and even those discontinued monitoring in 1995. These analyzers also measured methane (and non-methane hydrocarbons by subtraction) but the chromatographic separation of the methane was unreliable. The magnitude of the THC concentrations varies from site to site but the diurnal patterns are usually similar to those of CO and NO_X. Because of the limited nature and quality of the THC data from continuous monitoring, diurnal profiles are only presented for 1994 at Los Angeles-N. Main (Figures 2.1-88 and 2.1-89). The concentration scale is not zero-based to better display the anthropogenic variations.

2.1.4.5.1 Day-of-Week Characteristics

Although THC concentrations are lower during the summer than during winter (Figure 2.1-88), day-of-week patterns are still apparent in the diurnal profiles (Figure 2.1-89). THC concentrations are lowest on Sunday with the difference being most obvious during the morning and evening commute periods and into the late evening. Saturdays tend to have slightly lower concentrations than the weekdays and the diurnal profile is generally closer to that on weekdays than on Sundays. Saturday afternoon concentrations are very similar to the weekday concentrations. There is some evidence of variability among weekdays with Fridays exhibiting the peak concentrations during the morning commute and Mondays and Fridays tending to exhibit the highest concentrations during the evening. This is consistent with the common perception that driving activity is higher on Friday evenings.

2.1.4.5.2 Diurnal Characteristics

THC concentrations increase during the early morning hours and peak during the morning commute period. With photochemistry active and improving atmospheric dispersion, the THC concentrations begin to decline by 8 a.m. and reach a minimum about mid-afternoon.

At mid-day, the THC concentrations were indistinguishable from any other day of the week. In general, the Sunday concentrations were lower than other days except during the midnight to 4 a.m. period (when they were slightly higher than weekday concentrations).

With the evening commute and more stable atmospheric conditions, THC concentrations tend to increase in the evening. Evening THC concentrations tended to be higher on Monday and Friday.

2.1.5 Conclusions

These analyses were not designed to specifically test the five hypotheses of factors contributing to the observed ozone weekend effect. However, some of the spatial, diurnal, and annual differences lend more support to some hypotheses than to others.

Despite a large increase in VMT, concentrations of VOCs, NOX, and CO declined from 1994 to 1998. This decline occurred on weekdays as well as weekends. The decline in ozone concentrations on Sundays was less than the ozone decline on Saturdays (which was comparable to that of weekdays). Thus, NO_X reductions did not cause peak ozone concentrations to increase. However, the ozone reduction on Sundays may have been lessened by the dramatic reduction in NO_X during the morning commute period on Sundays.

Carryover in the surface layer of the atmosphere from one evening to the next morning does not appear to be a significant factor in the Weekend Effect. Carryover of ozone from Saturday evening into Sunday morning occurs primarily at non-urban sites. These sites tend not to experience rapid ozone build-up during the morning hours. The generally faster build-up of ozone on Sundays throughout much of the air basin appears more related to the lower NO_X concentrations and fewer radicals being terminated with NO_X reactions.

Ozone concentrations at many sites in the air basin tended to peak a little later in 1998 than in 1994. This pattern is consistent with hydrocarbon emissions being reduced and becoming less reactive. Ozone concentrations on Sunday in 1998 tended to peak earlier than on weekdays in the western portion of the SoCAB and to peak later than on weekdays in the eastern portion of the basin.

Both CO and NO_X concentrations exhibited lower concentrations on Sunday morning and, to a lesser extent, Saturday morning than on weekday mornings. However, weekend afternoon concentrations, particularly on Saturday, approach the concentration levels observed on weekdays. This pattern tends not to support the Increased Weekend Emissions hypothesis (although a spatial shift is involved) but is consistent with the NO_X-Timing hypothesis.

Both CO and NO_X concentrations exhibited a tendency for higher concentrations on Friday evening and, to a lesser extent, Saturday evening than on weekday evenings. However, the CO and NO_X concentrations generally return to typical levels

by 4 a.m. PST. This pattern indicates that carryover in the surface boundary layer probably is not a contributing factor to the Ozone Weekend Effect. However, more analysis of good quality data is needed to confirm this for hydrocarbon concentrations.

Morning NO_2/NO ratios are typically higher on Sundays, and to a lesser extent on Saturdays, than on weekdays at almost all sites. This pattern indicates a chemical environment in which ozone production can occur rapidly with the addition of NO_X and is consistent with the NO_X-Timing hypothesis. Although NO_2 concentrations are typically lower on Sundays, the NO_2/NO ratio is higher because the NO concentrations typically decline proportionately more than the NO_2 concentrations do. NO_2 concentrations peak a little earlier on weekends than on weekdays at most sites. This is consistent with ozone concentrations peaking earlier on weekends than on weekdays in the western portion of the SoCAB. However, as noted earlier, ozone concentrations in the eastern portion of the SoCAB peaked later on weekends than on weekdays. This indicates that the chemical regime might be slightly different on weekends, especially Sunday, than on weekdays.

2.1.6 Recommendations

Analysis of diurnal profiles during 1994 and 1998 in the SoCAB has identified several interesting features with potential insights into the Weekend Effect. Additional work is needed to refine the analyses and confirm the significance of the differences observed. We recommend the following additional efforts.

1) *Extend the diurnal analysis to other years.* Diurnal profiles of pollutant concentrations and ratios tend to be similar only during the mid-week (Tuesday-Thursday) and to have subtle but significant differences among the other days of the week. It is important that additional years are included in the analysis to reduce the influence of meteorological differences, which may have influenced the results for 1994 and 1998. Because the May through October period has a maximum of 26 samples for any given day of the week, the analysis periods should cover two or three years to reduce the uncertainties caused by meteorological variability. In addition, emission controls over the years have dramatically reduced ozone concentrations during the month of October. Further, the earlier and stronger surface inversions that occur during the second half of October can exert a disproportionate influence on the summer averages. A mid-May through mid-October or a June through September analysis would help focus the results on the heart of the ozone season and reduce the influence of changing meteorological regimes on the CO and NO_X concentrations in particular. Furthermore, it is important to recognize the apparently strong influence of the introduction of cleaner burning gasoline and separate the analysis into periods before 1995 and after 1996.

2) *Extend the diurnal analysis to other geographic areas.* Because the Ozone Weekend Effect apparently is not the same in all regions of California, it is important to expand these diurnal analyses of ozone precursors into other major populated areas of California (i.e., the San Diego, San Francisco Bay Area, San Joaquin

Valley, and Sacramento Air Basins). These areas have significantly different features (distribution of population and emissions, geography, meteorology) which could yield additional insights into why the Ozone Weekend Effects vary from area to area. A limiting factor for analyses in these areas however will be the reduced density of the monitoring network.

3) *Collect continuous HC data so temporal variations associated with this important ozone precursor can be constructed.* With the advent of Photochemical Assessment Monitoring Stations (PAMS), the antiquated continuous HC monitors in the SoCAB were decommissioned in 1995. For the most part, quantitative problems with these measurements (particularly, for methane and therefore NMHC because of difference by subtraction), limited the utility of these data for assessing trends, diurnal variations, NMHC/NO_X ratios, etc. With PAMS monitoring, crude diurnal profiles can be generated from the continuous speciated HC concentrations (3-hour averages measured by automated gas chromatography). However, the PAMS analysis is limited to 55 compounds and the results do not always represent the total mass of NMOCs or THCs. After some initial problems, this database is being built-up sufficiently for diurnal and day-of-week analyses. However, we believe that it is important to have at least two or three sites operating with continuous THC and methane measurements to track the short and long term temporal variations in overall NMHC and THC. Even more critically in light of the significance of NMHC/NO_X, it is crucial to the assessment of the Weekend Effect to have a clear understanding of how this ratio varies (especially diurnally among sub-regions) to critically scrutinize the hypotheses suggested for causing or contributing to the observed Weekend Effect.

4) *Apply multivariate statistical techniques to test specific statistical hypotheses suggested by some diurnal plots.* Many of the diurnal plots are suggestive of a variety of day-of-week differences and these apparent differences need to be further investigated and tested for their significance.

5) *Partition the data into days with high and low ozone concentrations and compare.* The first technical chapter includes an analysis of the Weekend Effect (for ozone) when days were segregated into groups of high, medium, and low ozone concentrations. Similar analyses could also be performed for the CO, NO_X, and NO_2/NO data.

6) *Investigate the relationship between diurnal profiles and traffic flows and vehicle activity in the vicinity of monitors.* An initial analysis of this relationship is included in the activity technical chapter and further work might not be necessary.

7) *Investigate sites in relation to local topography and emissions sources to see if patterns exist among sites affected by similar topography and emissions (e.g., sites impacted by weekend recreational activities nearby, sites near stationary sources operating on day-of-week schedules).* Emissions and activity patterns not only change hourly by day of the week but also spatially. Additional analysis of data at sites with distinctly different activities from workday to weekend needs to be

performed to gain additional insights into factors influencing the Weekend Effect. For example, sites in an urban/business core might be expected to have different activity and concentration patterns than sites in or along corridors to distant recreational centers. An urban site might experience the most traffic congestion during weekday commute periods while the recreational site might experience the most traffic congestion on a weekend morning or evening.

2.1.7 References

Austin, J., H. Tran (1999) "A Characterization of the Weekday-Weekend Effect Behavior of Ambient Ozone Concentrations in California," ARB staff analysis available at http://www.arb.ca.gov/aqd/weekendeffect/weekendeffect.htm.

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